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REVERSIBLE METAL-TO-METAL METHYL TRANSFER IN
η^5-CYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)DIMETHYLCOBALT(III)

Henry E. Bryndza, Eric R. Evitt, and Robert G. Bergman

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DISCLAIMER

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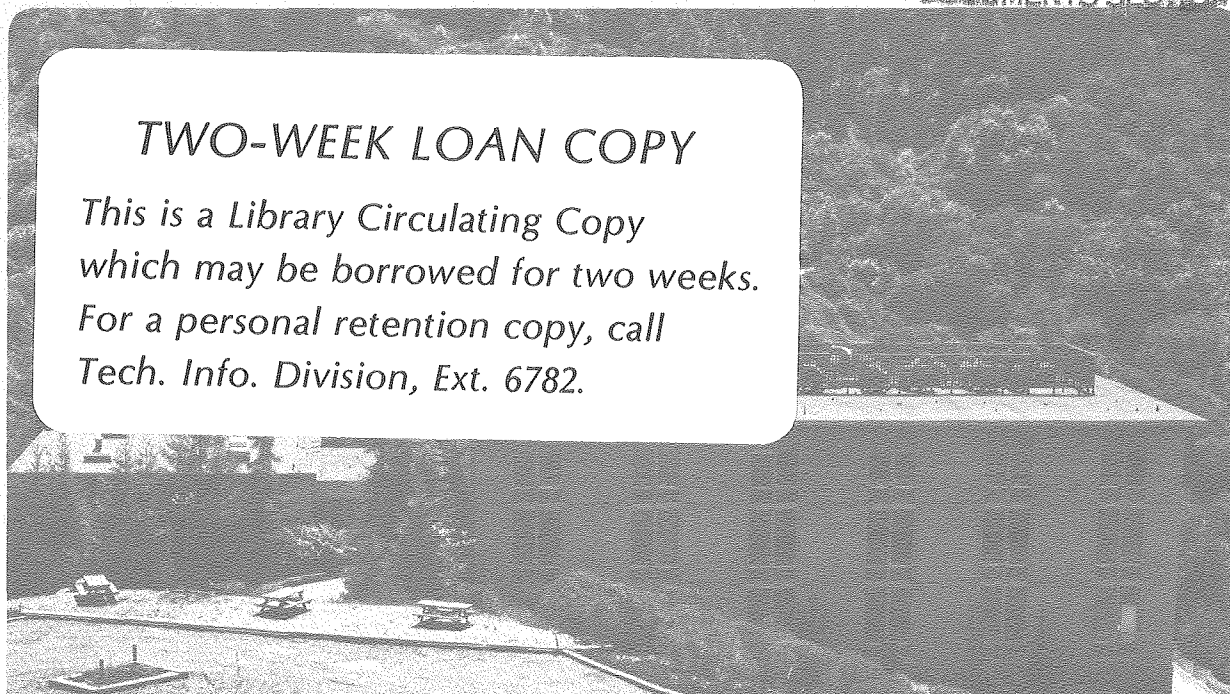
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Abstract

Labeling techniques have been used to demonstrate that η^5-cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (1) undergoes intermolecular cobalt-to-cobalt methyl group exchange. The reaction follows second order kinetics; rate constants for methyl exchange between complexes 1 and its methylcyclopentadienyl analog 4 show decreasing magnitude with increasing bulk of cyclopentadienyl substituents. Studies of the reaction with excess triphenylphosphine and complexes labeled with the non-dissociating trimethylphosphine ligand indicate the reaction requires dissociation of phosphine from one of the two partners in the exchange before scrambling can take place. Further studies with other complexes (e.g., $Cp_2Zr(CH_3)_2$) suggest that alkyl exchange between two transition metal centers may be a more general reaction than has heretofore been suspected.

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Introduction

One of the most ubiquitous ways carbon-metal bonds can be formed and broken invoves transfer of alkyl groups from one metal to another. Alkyl transfers from main-group to transition metal atoms have been known for many years, and there are now several examples of alkyl transfer between transition metal atoms.

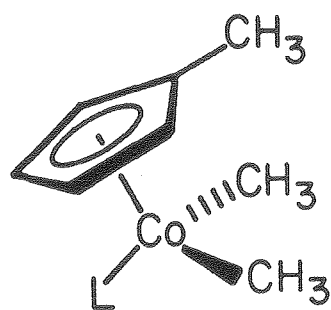Normally the characteristics of these transfer reactions can be easily classified as to their electronic character. For example, transfers of alkyl groups from main group alkyl reagents to metal halides[2], or vitamin B_{12}-analog cobalt alkyls to higher oxidation-state metals[3], can be thought of as involving transfer of an essentially nucleophilic alkyl to an electrophilic metal center. Alkyl transfer from Co(II) species to other metals are normally considered to be radicaloid substitution reactions[4]. Certain types of alkyl transfer reactions, however, are more difficult to classify. Among the most interesting of these are transfer of alkyl groups between similar (or identical) metal centers. Often these reactions (e.g., the interconversion of alkylplatinum halides with dialkyl- and dihaloplatinum complexes[5]; alkyl exchange involving zirconium and aluminum complexes[6]) involve situations in which the transfer of an alkyl group to the (electrophilic?) metal center is assisted by the simultaneous reverse transfer of halogen or other (nucleophilic?) ligand in the opposite direction.

However, a few stable symmetrically bridging dimeric organotransition metal complexes, in which alkyls bridge two metals without assistance of a nucleophilic ligand, are now
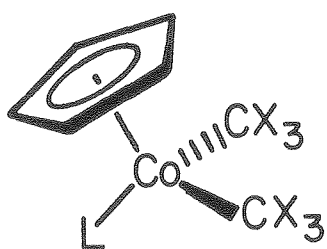
1 , L = PPh$_3$, X = H
1-d$_6$, L = PPh$_3$, X = D
3 , L = PMe$_3$, X = H
3-d$_6$, L = PMe$_3$, X = D

2 , L = PPh$_3$
4 , L = PMe$_3$

$$\text{Co(CO)}_2 \quad \text{CH}_2 \quad \text{Co(CO)}_2$$

$$\xrightarrow[70°]{\text{CO}}$$

$$CH_3-\overset{\overset{\textstyle O}{\|}}{C}-CH_3 \; +$$

$$H_3C-Co, \quad Co-CH_3 \qquad \underset{\sim}{5}$$

4
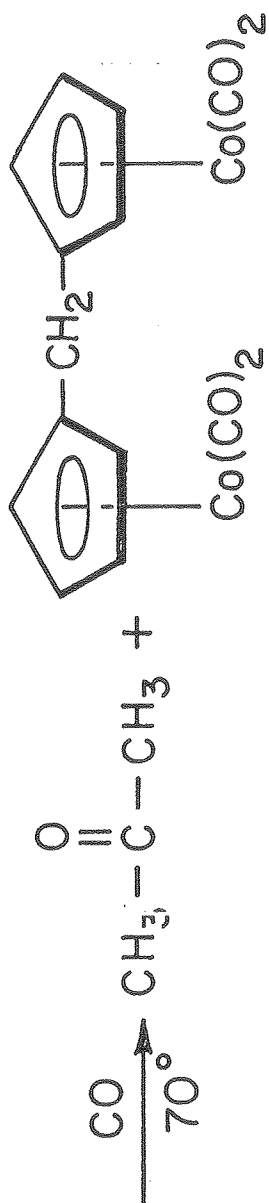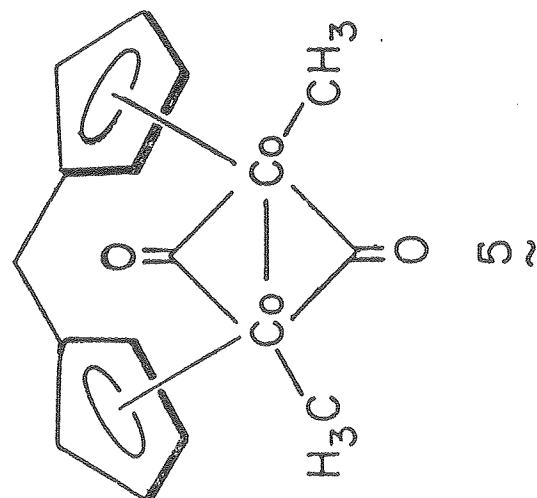
known[7]. This suggests bridging alkyls might be accessible as transition states or short-lived intermediates from many other stable underlined metal alkyls. We have now found that this is apparently true in η^5-cyclopentadienyltriphenylphosphine-(dimethyl)cobalt, a complex known for almost 15 years[8], where degenerate methyl transfer occurs easily at 60°C. In this paper we report the results of a mechanistic study of this symmetrical alkyl transfer reaction. Our results indicate that an unsaturated site on one of the two participating centers is required, and we have collected information about the effect of phosphine and cyclopentadiene substituents on the reaction rate.

Results

Alkyl exchange involving the $RCpCo(L)Me_2$ moiety was first implicated during a control experiment designed to investigate the molecularity of the carbonylation of binuclear complex 5[9]. When a mixture of $5-d_0$ and $5-d_6$ (labeled methyl groups) was carbonylated at high (0.25 M) concentrations at 70°C with 5 atmospheres of CO, the acetone produced was partly (ca 30%) d_3- in addition to the expected d_0- and d_6-acetones. Carbonylation of mixtures of 1 and $1-d_6$ at higher concentrations (0.25 M) showed alkyl crossover similar to that seen with 5. As reported elsewhere[10], carbonylation of 1 and $1-d_6$ at moderate concentrations (0.05 M) yields only d_0- and d_6-acetones. Heating a 0.25 M mixture of 1 and $1-d_6$ at 60°C for 40 hr. without CO, followed by dilution to 0.05 M and treatment with CO under conditions previously established to preclude crossover during carbonylation, gave a statistical ratio of d_6-, d_3-, and d_0-

acetone. Clearly the scrambling reaction was taking place in a prior process unconnected with the carbonylation.

In order to study the alkyl transfer directly by ^{1}H NMR, we prepared the methylcyclopentadienyl analog 2; preliminary measurements demonstrated that the cobalt-bound methyl resonances of 1 and 2 could be resolved cleanly. When equal amounts of 1-d_6 and 2 were dissolved in THF-d_8 and heated in a sealed NMR tube at 61.7^{O}C a new methyl doublet, corresponding to the resonance observed for 1, was seen growing into the NMR spectrum at the expense of the original methyl doublet of 2 . Addition of excess triphenylphosphine was found to reduce the rate of scrambling. In order to further study the role of phosphine in this exchange, the trimethylphosphine analogs 3 and 4 were prepared. In contrast to PPh$_3$, the rate of dissociation of PMe$_3$ from the cobalt center in these complexes is known[10] to be negligible at temperatures near 60°C. The reaction of 1-d_6 with 4 was found to again exchange methyl groups at 62°C, but the rate was reduced to somewhat less than half that associated with interchange involving 1 and 2 at that temperature. Heating 3-d_6 in the presence of 4 at 62°C showed no evidence of scrambling. These results clearly indicate that dissociation of phosphine from one metal center is both necessary and sufficient for exchange to take place.

Because there are a large number of (in principle) chemically distinguishable species involved in these exchange processes (see Scheme 1), and each step is reversible, the kinetics required to describe them are complex. Assuming for the

moment that we may ignore secondary isotope effects, each system [(a), (b), and (c) in Table 1] is characterized by six different exchange equilibria (Scheme 1) but only three different phenomenological rate constants. The fact that no exchange is observed in system (c) requires that k_3 in systems (c) and (b) [which is the same rate constant as k_3 in system (c)] be effectively zero under our reaction conditions. Similarly, k_1 is associated with the same process in systems (a) and (b). Using this type of reasoning, one may reduce the set of nine rate constants in Table 1 to four which are essentially zero and five which need to be determined; two of the five are identical. An additional complication arises from the fact that our NMR analysis does not measure the concentrations of the individual complexes, but rather the total "concentration" of methyl groups bound, for example, to CpCo, and separately the "concentration" of methyl groups bound to MeCpCo. The ratio 'R' plotted against time in figures 1 and 3 is simply the former "concentration" (methyl groups bound to CpCo) divided by the total "concentration" of all metal bound methyl groups.

We were able to satisfactorily model the variations in 'R' vs time (figure 1) by the use of an interactive mechanism simulation computer program[11]. This program takes rate constants and reaction steps as input material, and through probability calculations based on concentrations, rate constants and frequency of a given step, simulates the series of reactions and calculates the concentrations of individual species with time.

For the case of system (a), the ratio 'R' is:

$$R = \frac{[1-d_3] + 2[1-d_0]}{[1-d_3] + 2[1-d_0] + [2-d_3] + 2[2-d_0]}$$

This, given all the individual concentrations, is calculated and plotted against time. The rate constants are then varied until the fit is optimized. To save time, initial rate constants are estimated by assuming that at short reaction times reaction (5) in Scheme 1 is the only important step (due to insignificant concentrations of other species initially) and calculating the second order rate constant for that step from the data. Reactions involving k_1 or k_3 are less frequent than those involving k_2 because of concentrations of species involved as well as the sheer number of steps involving k_2 in the mechanism outlined in Scheme 1. Therefore, k_1 and k_3 affect the overall fit less than k_2, and that latter rate constant was optimized first followed by the optimization of k_1 and k_3. An obvious consequence of this method is that k_1 and k_3 are known with less accuracy than k_2. The rate constants thus calculated can be found in Table 1 while sample fits are ilustrated in Figure 1. The satisfactory nature of the fit indicates that the reaction follows second order kinetics and that our initial assumption, that secondary isotope effects are negligible within our experimental error, is valid. The effects of varying the rate constants on the fit can be seen in Figure 2.

Discussion

With these rate constants in hand, we can draw some preliminary conclusions about the mechanism of the exchange

reaction. The effect of changing PPh_3 concentrations on the exchange rate, the fact that two PMe_3 complexes react so slowly, and mechanistic studies of other reactions[10] of dialkyl 1, indicate that the exchange requires initial dissociation of phosphine. The fact that the PMe_3 complex will transfer methyl groups to a PPh_3 complex, but not to a second PMe_3 complex, indicates each exchange step takes place between one complex which has lost a phosphine and a second complex which has not. The decrease in magnitude in going from k_1 to k_2 to k_3, the decrease in rate with increased phosphine concentration, and dissociation rates in other systems[10] all suggest that phosphine is lost in a rapid pre-equilibrium step, followed by rate-determining combination of the second complex with the unsaturated intermediate so generated, as shown in Scheme 2. It seems reasonable that the binuclear transition state involved in this second step is destabilized by steric repulsions between methyl groups on the cyclopentadienyl rings. In order to interconvert states A and C any intermediate or transition state must account for the reversible methyl exchange observed. By cleavage in either of two possible ways, a transition state or intermediate having structure B fulfills these requirements. Precedent for B in non-transition metal alkyl exchanges and particularly the known stable transition metal complexes with bridging alkyl groups[7] make it the attractive intermediate. Whatever the transition state actually is, clearly this exchange is significantly different in nature from both exchanges involving anionic supernucleophile Co^I and Rh^I porphyrins, and

the radicaloid alkyl exchanges of Co^{II} systems. Both of those exchange mechanisms involve only one alkyl group per pair of metal complexes and the net effect is never alkyl scrambling among thermodynamically equivalent species. Rather, this exchange shows striking similarities to many substitution reactions involving other (halogen, hydride and mixed alkyl/halo) ligands and to main group/transition metal alkyl exchanges. Its dependence upon the unsaturated (and perhaps electrophilic) character of one partner may prove more general as further mechanistic information becomes available.

The facile exchange of alkyl groups in otherwise stable metal alkyls bodes caution for crossover experiments designed to probe the important mechanistic question of molecularity during reactions of those species. In extensions of the results outlined above, we have obtained preliminary evidence that alkyl exchange between transition metal centers may be a more general process than has heretofore been suggested. Thus, although $1-d_6$ and Cp_2MoMe_2 do not exchange methyls, we do observe such exchange between $1-d_6$ and Cp_2ZrMe_2. Further research will be required to define more precisely the scope of these reactions, the factors which control their efficiency, and the nature of the exchange transition state.

Experimental Section

General

All manipulations of oxygen or water sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Tetrahydofuran (THF) and diethyl ether were distilled from purple sodium/benzophenone ketyl solutions. Benzene and hexanes were degassed and used as supplied from J.T.Baker ("Analyzed Reagent" grade). PPh_3 (MCB) was recrystallized twice from hexanes and dried overnight under high vacuum. Methylcyclopentadiene was freshly distilled at atmospheric pressure from the commercially available (Aldrich) dimer and stored at $-78^{\circ}C$ until used.

Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283 grating spectrophotometer using solutions of samples in sodium chloride cells (0.10 mm path length).

Elemental analyses were conducted by the U.C.Berkeley analytical facility.

NMR Experiments

[1]H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 spectrometer. Spectra are reported in units of ppm downfield from tetramethylsilane, but were most often measured relative to residual ^{1}H absorption in deuterated solvent: benzene-d_6(7.15), THF-d_8(1.73), and acetone-d_6(2.04). Deuterated THF and benzene were vacuum transferred from ketyl solutions while acetone-d_6 was transferred off of Linde 4A$^{\circ}$

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molecular sieves and degassed with three freeze-pump-thaw cycles on a vacuum line.

NMR experiments were carried out as follows: a standard NMR tube fused to a 14/20 ᵀ ground glass joint was loaded with the desired compounds in the dry box, capped with a teflon needle valve, placed on a vacuum line, and evacuated. The tube was charged with the desired amount of solvent by vacuum transfer out of a graduated tube of solvent. The tube was then sealed and carefully thawed before being heated in a refluxing $CHCl_3$ bath. Spectra were recorded by removing the tube from the bath after the desired elapsed time, plunged into ice water (none of the reactions proceeded at measurable rates below $55^{\circ}C$) and placed in the NMR probe when dry. The spectrum was recorded and the tube replaced in the constant temperature bath.

Syntheses

$CpCo(PPh_3)(CH_3)_2$, $CpCo(PPh_3)(CD_3)_2$, and $CpCo(P(CH_3)_3)(CD_3)_2$ were prepared by previously published methods[6c]. Methyl cyclopentadienyl analogs were prepared by the same methods used to prepare the unsubstituted cyclopentadienyl analogs. Structures of previously known compounds were established by comparison of spectral data with those reported earlier; new compounds were characterized by standard spectral and analytical techniques. Data for new compounds follow:

$(C_5H_4CH_3)Co(CO)I_2$: NMR ($CDCl_3$/TMS): 5.42(s,4H); 2.50(s,3H). IR(Et_2O): 2065 cm^{-1}. Anal: Calculated for $C_7H_7CoI_2O$: C(20.02%); H(1.68%); Co(14.04%); I(60.45%). Found: C(20.22%); H(1.78%); Co(13.1%); I(60.48%). $(C_5H_4CH_3)Co(PPh_3)I_2$:

NMR(CDCl$_3$/TMS): 7.2-7.9(m,15H); 5.05(m,AA',2H); 4.15(m,BB',2H);
2.54(d,J=2.5Hz,3H). <u>Anal</u>: Calculated for C$_{24}$H$_{22}$CoI$_2$P:
C(44.07%); H(3.39%); Co(9.01%); I(38.80%); P(4.73%). Found:
C(43.85%); H(3.49%); Co(8.64%); I(39.02%); P(4.90%).
(C$_5$H$_4$CH$_3$)Co(PPh$_3$)(CH$_3$)$_2$: NMR(THF-d$_8$): 7.2-7.6(m,15H);
5.1(m,AA'BB',4H); 1.58(d,J=3Hz,3H); -0.05(d,J=5.5Hz,6H). <u>Anal</u>:
Calculated for C$_{26}$H$_{28}$CoP: C(72.55%); H(6.56%); Co(13.69%);
P(7.20%). Found: C(72.60%); H(6.55%); Co(14.0%); P(7.04%).
(C$_5$H$_4$CH$_3$)Co(P(CH$_3$)$_3$)(CH$_3$)$_2$:   NMR(THF-d$_8$):   5.05,
5.30(m,AA'BB',4H); 2.35(s,3H); 2.25(d,J=9Hz,9H); -
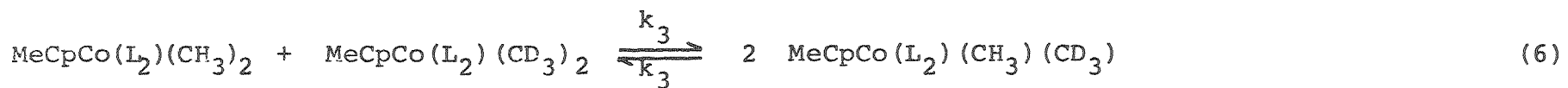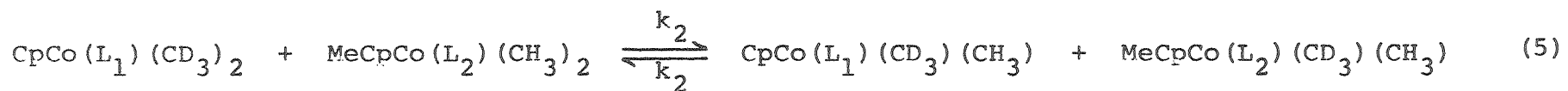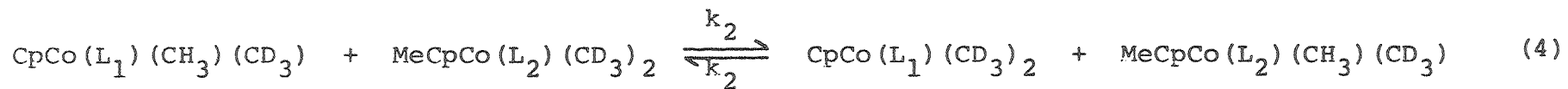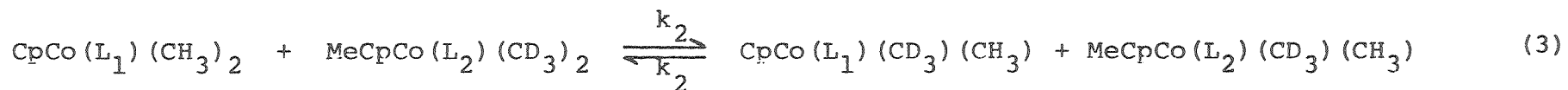0.30(d,J=6Hz,6H).

Acknowledgements

References and Notes

1) Hertz Foundation Fellow, 1977 to present.

2) For leading references regarding the extensive body of literature dealing with alkylation reactions see: a) Heck, R. F., Organotransition Metal Chemistry, Academic Press, New York, 1974, Ch. 2-Part B; b) Coates, G. E.; Green, M. L. H.; Wade, K., Oranometallic Compounds, Volume 2, 3rd ed., Chapman & Hall, London, 1968, Ch. 7; c) Sinn, H.; Opermann, G., Angew. Chem. 1966, 78, 986.

3) See, for example: a) Dodd, D.; Johnson, M. D., J. Chem. Soc., Chem. Commun. 1971, 1371; b) Costa, G.; Mestroni, G.; Cocevar, C., J. Chem. Soc., Chem. Commun. 1971, 1869; c) Costa, G.; Puxeddu, A.; Reisenhofer, E., J. Chem. Soc., Dalton Trans. 1972, 1519; d) Halpern, J., Ann. N. Y. Acad. Sci. 1974, 239, 2; e) Andeson, S. N.; Balard, D. H.; Chrzastowski, J. Z.; Dodd, D.; Johnson, M. D., J. Chem. Soc., Chem. Commun. 1972, 685; f) Dodd, D., Johnson, M. D.; Lockman, B. L., J. Am. Chem. Soc. 1977, 99, 3664.

4) See for example Ref 2d or: a) Van den Bergen, A.; West, B. O., J. Chem. Soc., Chem. Commun. 1971, 52; b) Van den Bergen, A.; West, B. O., J. Organomet. Chem. 1974, 64, 125; c) Espenson, J. H.; Sellers, T. D. Jr., J. Amer. Chem. Soc. 1974, 96, 94; d) Espenson, J. H.; Leslie, J. P. II, J. Am. Chem. Soc. 1974, 96, 1954; e) Espenson, J. H.; Shveima, J. S., J. Am. Chem. Soc. 1973, 95, 468.

5) For examples of alkyl transfer between transition metals which is assisted by a potentially bivalent bridging group (e.g., halogen, CH_2) see: (a) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood J. L.; Hunter, W. E., J. Chem. Soc., Chem. Commun. 1976, 480; (b) Puddephatt, R. J.; Thompson, P. J., J. Chem. Soc., Dalton Trans. 1975, 1810; (c) Thompson, P. J.; Puddephatt, R. J., J. Chem. Soc., Chem. Commun. 1975, 841; (d) Dodd, D.; Johnson, M. D., J. Chem. Soc., Chem. Commun. 1971, 1371; (e) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E., J. Chem. Soc., Dalton Trans. 1979, 45; (f) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E., J. Chem. Soc., Dalton

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8)   (a) King, R. B.,_Inorg. Chem._ 1966, 5, 82; (b) Yamazaki, H.; Hagihara, N.,_J. Organomet. Chem._ 1970, 21, 431.

9)   Bryndza, H. E.; Bergman, R. G.,_J. Am. Chem. Soc._ 1979, 101, 4766.

10)   The thermal decomposition of 1 as well as the reactions of 1 with PhCCPh, C_2H_4 and CO all demonstrate an inverse dependence of reaction rate upon phosphine concentration. See for example: (a) Evitt, E. R.; Bergman, R. G.,_J. Am. Chem. Soc._ 1978, 100, 3237; (b) Evitt, E. R.; Bergman, R. G.,_J. Am. Chem. Soc._ 1979, 101, 3973; (c) Evitt, E. R.; Bergman, R. G.,_J. Am. Chem. Soc.,_ submitted.

11)   Program MSIM4 developed by D. L. Bunker and F. Houle, Univ. of Calif., Irvine, CA and available from the Quantum Chemistry Program Exchange (Program #293).
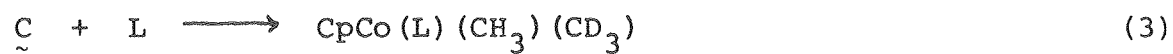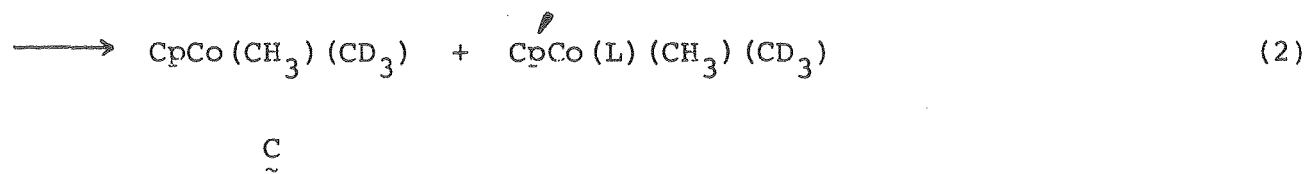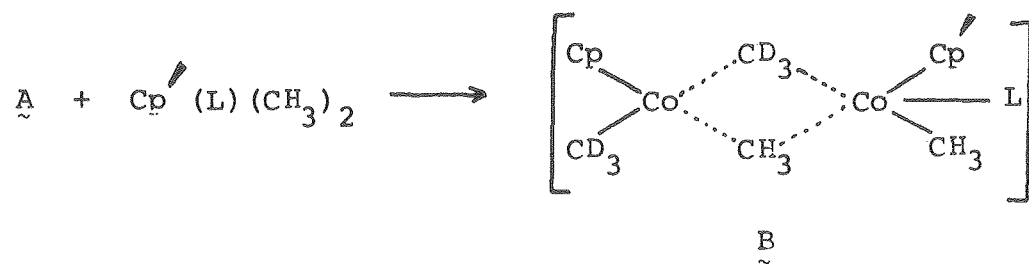
Scheme I

$$CpCo(L_1)(CH_3)_2 \; + \; CpCo(L_1)(CD_3)_2 \; \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \; 2 \; CpCo(L_1)(CH_3)(CD_3) \tag{1}$$

$$CpCo(L_1)(CH_3)_2 \; + \; MeCpCo(L_2)(CH_3)(CD_3) \; \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \; CpCo(L_1)(CD_3)(CH_3) \; + \; MeCpCo(L_2)(CH_3)_2 \tag{2}$$

$$CpCo(L_1)(CH_3)_2 \; + \; MeCpCo(L_2)(CD_3)_2 \; \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \; CpCo(L_1)(CD_3)(CH_3) \; + \; MeCpCo(L_2)(CD_3)(CH_3) \tag{3}$$

$$CpCo(L_1)(CH_3)(CD_3) \; + \; MeCpCo(L_2)(CD_3)_2 \; \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \; CpCo(L_1)(CD_3)_2 \; + \; MeCpCo(L_2)(CH_3)(CD_3) \tag{4}$$

$$CpCo(L_1)(CD_3)_2 \; + \; MeCpCo(L_2)(CH_3)_2 \; \underset{k_2}{\overset{k_2}{\rightleftharpoons}} \; CpCo(L_1)(CD_3)(CH_3) \; + \; MeCpCo(L_2)(CD_3)(CH_3) \tag{5}$$

$$MeCpCo(L_2)(CH_3)_2 \; + \; MeCpCo(L_2)(CD_3)_2 \; \underset{k_3}{\overset{k_3}{\rightleftharpoons}} \; 2 \; MeCpCo(L_2)(CH_3)(CD_3) \tag{6}$$

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Scheme 2

$$CpCo(L)(CD_3)_2 \rightleftharpoons \underset{\underset{\sim}{A}}{CpCo(CD_3)_2} + L \qquad (1)$$

$$\underset{\sim}{A} + Cp'(L)(CH_3)_2 \longrightarrow \begin{bmatrix} Cp & \overset{CD_3}{\underset{CH_3}{\diagdown}} & Cp' \\ CD_3 & Co & CH_3 \\ & \underset{\sim}{B} & \end{bmatrix} \qquad$$

$$\longrightarrow \underset{\underset{\sim}{C}}{CpCo(CH_3)(CD_3)} + Cp'Co(L)(CH_3)(CD_3) \qquad (2)$$

$$\underset{\sim}{C} + L \longrightarrow CpCo(L)(CH_3)(CD_3) \qquad (3)$$

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Table 1. Rate Constants for Methyl Exchange Reactions Shown in Scheme 1 (Solvent: THF-d_8)

		Rate constants[a] (M^{-1} sec^{-1})		
System	Ligands	k_1[b]	k_2[c]	k_3[b]
(a)	$L_1 = L_2 = PPh_3$	3.6×10^{-3}	2.2×10^{-4}	8.3×10^{-6}
(b)	$L_1 = PPh_3$, $L_2 = PMe_3$	3.6×10^{-3}	8.6×10^{-5}	0
(c)	$L_1 = L_2 = PMe_3$	0	0	0

[a]Starting concentrations of cobalt complexes in each case are 0.175 M. [b]Value ± 10%. [c]Value ± 0.5%.

Figure Captions

Figure 1. Computer simulation of the rate of methyl exchange in the reaction between $1\text{-}d_6$ and 2 ($\diamondsuit$) and between $1\text{-}d_6$ and 4 ($\bigcirc$). Diamonds ($\diamondsuit$) and circles ($\bigcirc$) are experimental data; solid lines are calculated using the rate constants shown in Table 1. The function R plotted on the abcissa is the ratio of integrated metal-bound methyl absorption in the Cp-substituted complex in each reaction, divided by the total CH_3 integration (metal-bound methyls in Cp-substituted plus MeCp-substituted complexes).

Figure 2. Effects of variations in k values on fit of data for case (a) of Table 1. Line (a) shows best fit line for the data points ($\bullet$). Line (b) shows result of variation of 2% in k_2 (k_1 and k_3 unchanged). Line (c) shows change in line caused by 20% variation in k_1 (k_2 and k_3 unchanged).

Figure 3. Plots of the ratio R (see Fig. 1 for definition of this ratio) vs. time for the following reactions: $\diamondsuit$ = $1\text{-}d_6$ with 2; $\bigcirc$ = $1\text{-}d_6$ with 4; $\square$ = $1\text{-}d_6$ with 2 containing excess (1.75 M) PPh_3; $\triangle$ = $3\text{-}d_6$ + 4.
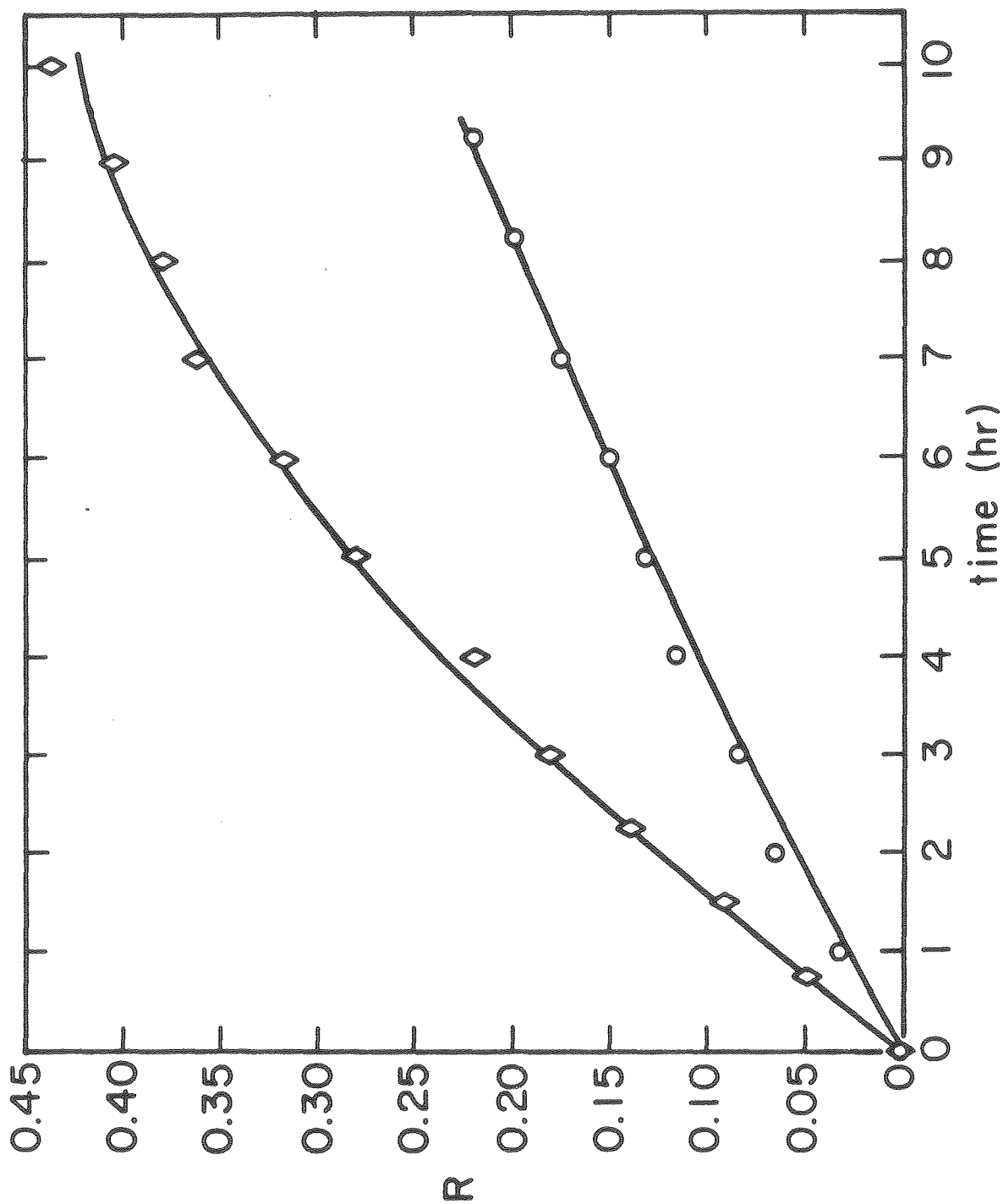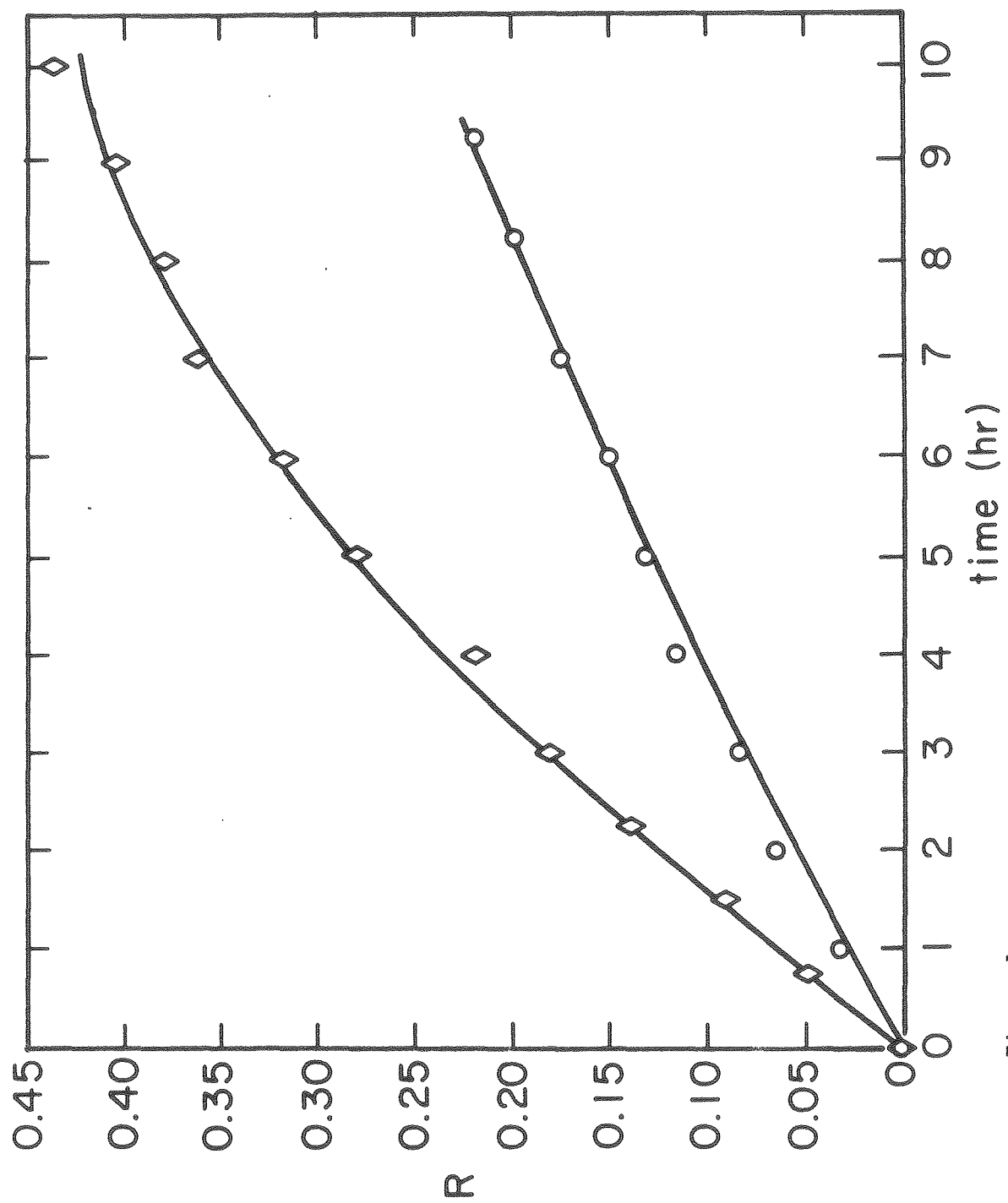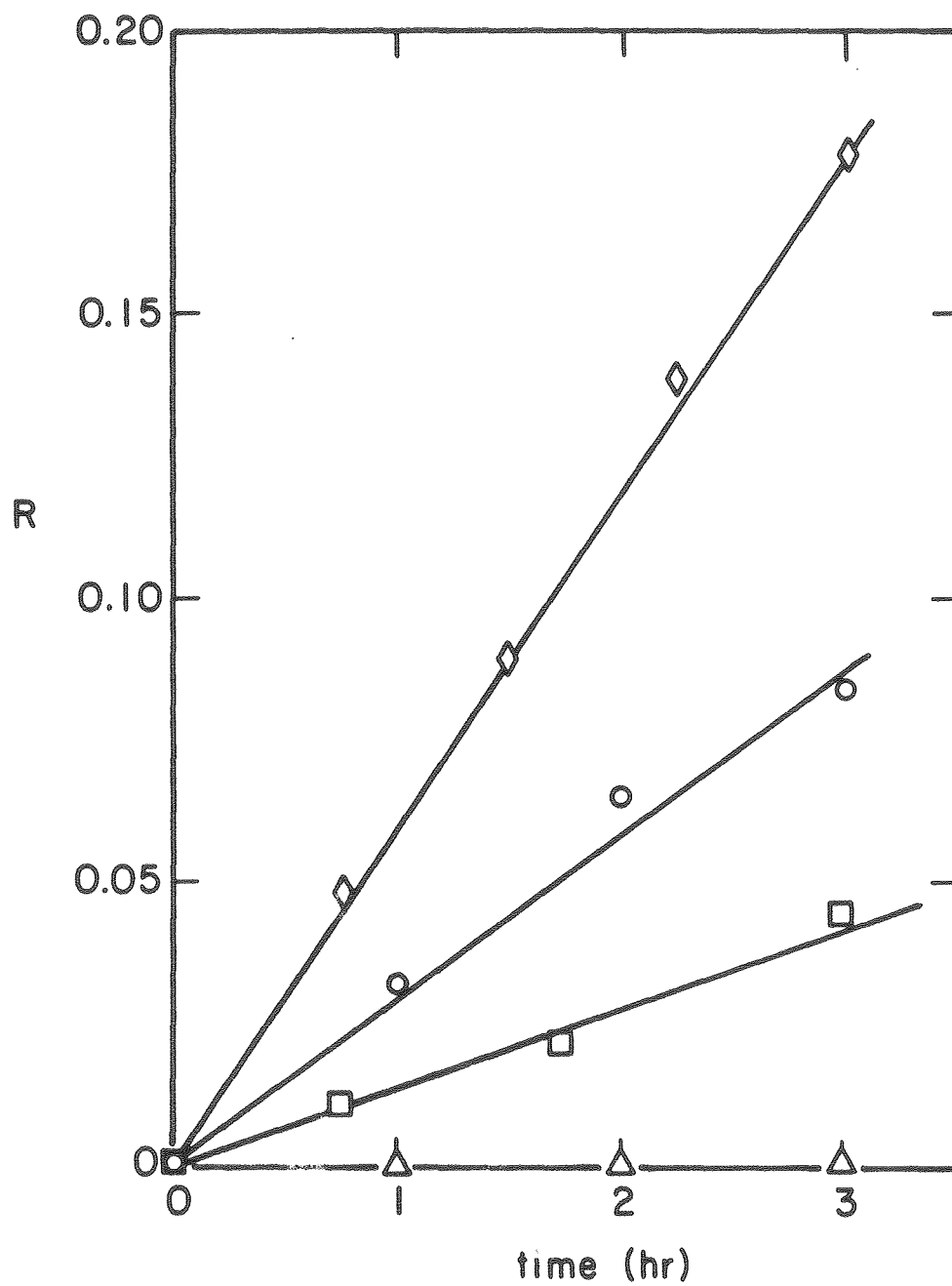
Figure 1

Figure 1

20

Figure 2

Figure 3

Figure 3